

# REPORT DOCUMENTATION PAGE

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14. ABSTRACT  Our AFOSR-supported research during the last three years focused on several experimental programs at the interface of ion spectroscopy and molecular reaction dynamics. We have developed a new method for high resolution photodetachment spectroscopy of negative ions based on photoelectron imaging (SEVI, or Slow photoElectron Velocity-map Imaging) and applied it to simple test systems as well as a pre-reactive van der Waals complex. We have measured photoelectron spectra of solvated transition state precursor anions, and used the vibrational structure in these spectra to infer the effect of various solvents on the strong hydrogen bond in the anion core. This work led to a series of experiments in which we measured the infrared spectra of several strongly hydrogen-bonded anions and the protonated water dimer H <sub>5</sub> O <sup>+</sup> . These experiments were performed on the Free Electron Laser for Infrared experiments (FELIX) which produces high power, tunable infrared pulses over a broad spectral range, enabling the first measurements of the low (<1000 cm <sup>-1</sup> ) frequencies associated with the large amplitude motion of the shared proton in these ions. Finally, we investigated the photodissociation dynamics of the ClN <sub>3</sub> molecule at 248 nm using molecular beam photofragment translational spectroscopy, determining that the "conventional wisdom" regarding its primary photochemical branching was totally incorrect.				
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## **1. FINAL TECHNICAL REPORT**

**TITLE:** Studies of Transition States, Cluster, and Radicals by Negative Ion Photodetachment and Photodissociation

**PRINCIPAL INVESTIGATOR:** Daniel M. Neumark

**DATE:** 2/1/03 – 1/31/06

**GRANT NO:** F49620-03-1-0085

**SENIOR RESEARCH PERSONNEL:** none, other than Principal Investigator

**JUNIOR RESEARCH PERSONNEL:** Mark Abel, Nathan Bartlett, Paul Crider, Etienne Garand, Scott Goncher, Graham Griffin, Aster Kammrath, Jeong Hyun Kim, Katherine Kautzman, Oleg Kornilov, Giovanni Meloni, David Moore, Matt Nee, Andreas Osterwalder, Bradley Parsons, Thomas Pfeifer, Sean Sheehan, Neils Sveum, David Szpunar, Jan Verlet, Chia Wang, Terry Yen, Jia Zhou,

**20060601080**

## **2. Objectives**

(unchanged)

## **3. Status of Effort (200 words)**

Our AFOSR-supported research during the last three years focused on several experimental programs at the interface of ion spectroscopy and molecular reaction dynamics. We have developed a new method for high resolution photodetachment spectroscopy of negative ions based on photoelectron imaging (SEVI, or Slow photoElectron Velocity-map Imaging) and applied it to simple test systems as well as a pre-reactive van der Waals complex. We have measured photoelectron spectra of solvated transition state precursor anions, and used the vibrational structure in these spectra to infer to effect of various solvents on the strong hydrogen bond in the anion core. This work led to a series of experiments in which we measured the infrared spectra of several strongly hydrogen-bonded anions and the protonated water dimer  $\text{H}_5\text{O}_2^+$ . These experiments were performed on the Free Electron Laser for Infrared experiments (FELIX) which produces high power, tunable infrared pulses over a broad spectral range, enabling the first measurements of the low ( $<1000 \text{ cm}^{-1}$ ) frequencies associated with the large amplitude motion of the shared proton in these ions. Finally, we investigated the photodissociation dynamics of the  $\text{ClN}_3$  molecule at 248 nm using molecular beam photofragment translational spectroscopy, determining that the "conventional wisdom" regarding its primary photochemical branching was totally incorrect.

## **4. Accomplishments/New Findings:**

A new technique for high resolution anion photodetachment spectroscopy was developed that combines velocity map imaging and anion threshold photodetachment. This method, Slow Electron Velocity-map Imaging (SEVI), provides spectral line widths of better than 1 meV. Spectra over a substantial range of electron kinetic energy are recorded in a single image, providing a dramatic reduction of data acquisition time compared to other techniques with comparable resolution. We applied this technique to atomic iodine and the van der Waals cluster  $\text{I}\cdot\text{CO}_2$  as test systems, and then to the pre-reactive  $\text{Cl}\cdot\text{D}_2$  complex where partially resolved structure assigned to hindered rotor motion was observed. High resolution anion photodetachment spectra were also obtained for the methoxide anion and its fully deuterated counterpart. The spectra were obtained with slow electron velocity-map imaging (SEVI). Improved electron affinities are determined for  $\text{CH}_3\text{O}$  as  $1.5690 \pm 0.0019 \text{ eV}$  and for  $\text{CD}_3\text{O}$  as  $1.5546 \pm 0.0019 \text{ eV}$ . The spectra resolve many features associated with spin-orbit and vibronic coupling that were not seen in previous photodetachment studies.

The Free Electron Laser for Infrared experiments (FELIX) was used to investigate strong hydrogen-bonds in cations and anions. The protonated water dimer is a prototypical system for the study of proton transfer in aqueous solution. We report infrared photodissociation spectra of cooled  $\text{H}^+(\text{H}_2\text{O})_2$  [and  $\text{D}^+(\text{D}_2\text{O})_2$ ] ions, measured

between 620 and 1900 cm<sup>-1</sup>. The experiment directly probes the shared proton region of the potential energy surface and reveals three strong bands below 1600 cm<sup>-1</sup> and one at 1740 cm<sup>-1</sup> (for H<sub>5</sub>O<sub>2</sub><sup>+</sup>). From a comparison to multidimensional quantum calculations, the three lower energy bands were assigned to stretching and bending fundamentals involving the O-H<sup>+</sup>--O moiety, and the highest energy band was assigned to a terminal water bend. These results highlight the importance of intermode coupling in shared proton systems.

In addition, gas phase vibrational spectra of BrHI<sup>-</sup> and BrDI<sup>-</sup> have been measured from 590–1666 cm<sup>-1</sup> in order to characterize the strong hydrogen bond in these species. BrHI<sup>-</sup>•Ar and BrDI<sup>-</sup>•Ar complexes were produced and mass selected, and the depletion of their signal due to vibrational predissociation was monitored as a function of photon energy. The spectra show numerous transitions, which had not been observed by previous matrix studies. New *ab initio* calculations of the potential-energy surface and the dipole moment are presented and are used in variational to-vibrational calculations to assign the spectral features. These calculations highlight the importance of basis set in the simulation of heavy atoms such as iodine. Further, they demonstrate extensive mode mixing between the bend and the H-atom stretch modes in BrHI<sup>-</sup> and BrDI<sup>-</sup> due to Fermi resonances.

Photofragmentation translation spectroscopy was used to identify the primary and secondary reaction pathways in the KrF laser (248 nm) photodissociation of chlorine azide (ClN<sub>3</sub>) under collision-free conditions. Both the molecular channel producing NCI ( $X\ ^3\Sigma$ ,  $a\ ^1\Delta$ ) + N<sub>2</sub> and the radical channel producing C1 ( $^2P_j$ ) + N<sub>3</sub> were analyzed in detail. Consistent with previously reported velocity map imaging experiments a bimodal translational energy distribution was seen when C1 atoms are monitored at  $m/z = 35$  (C1<sup>+</sup>). Momentum-matched N<sub>3</sub> counterfragments will be seen at  $m/z = 42$  (N<sub>3</sub><sup>+</sup>). The characteristics of the observed radical-channel data reflect the formation of linear azide radical and another *high-energy form* of N<sub>3</sub> (HEF-N<sub>3</sub>) that exhibits many of the characteristics one would expect from cyclic N<sub>3</sub>. HEF-N<sub>3</sub> could be directly detected by electron -impact ionization more than 100 μs after its formation. Products of the unimolecular dissociation of HEF-N<sub>3</sub> were observed in  $m/z = 14$  (N<sup>+</sup>) and  $m/z = 28$  (N<sub>2</sub><sup>+</sup>) data. Anisotropy parameters were determined for the primary channels to be  $\beta = -0.3$  for the NCI formatting channel  $\beta = 1.7$  and  $\beta = 0.4$  for the linear N<sub>3</sub> and HEF-N<sub>3</sub> forming channels, respectively. There was additional evidence for secondary photodissociation of N<sub>3</sub> and of NCI.

## 5. Personnel Reported

### Post-Docs

Jeong Hyun Kim  
Oleg Kornilov  
Giovanni Meloni  
David Moore  
Andreas Osterwalder  
Bradley Parsons  
Thomas Pfeifer  
Jason Robinson  
David Szpunar  
Jan Verlet

### Graduate Students

Mark Abel  
Paul Crider  
Etienne Garand  
Scott Goncher  
Graham Griffin  
Aster Kammrath  
Katherine Kautzman  
Sean Sheehan  
Niel Sveum  
Chia Wang  
Terry Yen  
Jia Zhou

### Undergraduate student

Nathan Bartlett  
Mason Gaffey  
James Madrid

### Visiting Graduate Students

Christer Bisgaard  
Department of Physics  
and Astronomy  
University of Aarhus  
Denmark

Nadine Wehres  
Heinrich-Heine-University  
Düsseldorf  
Germany

### High School Student

Jessica Lam

## 6. Publications

M. J. Ferguson, G. Meloni, H. Gomez, and D. M. Neumark, "Photoelectron spectroscopy of ClH<sub>2</sub><sup>-</sup> and ClD<sub>2</sub><sup>-</sup>: A probe of the Cl + H<sub>2</sub> van der Waals well and spin-orbit excited states" *J. Chem. Phys.* 117, 8181 (2002).

K. R. Asmis, N. L. Pivonka, G. Santambrogio, M. Brummer, C. Kaposta, D. M. Neumark, and L. Woste, "Gas-phase infrared spectrum of the protonated water dimer" *Science* 299, 1375 (2003).

N. L. Pivonka, C. Kaposta, M. Brummer, G. von Helden, G. Meijer, L. Woste, D. M. Neumark, and K. R. Asmis, "Probing a strong hydrogen bond with infrared spectroscopy: Vibrational predissociation of BrHBr<sup>-</sup>Ar" *J. Chem. Phys.* 118, 5275 (2003).

"H. Gomez, G. Meloni, J. Madrid, and D. M. Neumark," Anion photoelectron spectroscopy of solvated transition state precursors *J. Chem. Phys.* 119, 872 (2003).

D.M. Neumark, "Transition State Spectroscopy" *Advanced Series in Physical Chemistry*, vol. 14, Modern Trends in Chemical Reaction Dynamics (Part 1), ed. X. Yang and K. Liu, (World Scientific Publishing, Singapore, 2004) pp. 435-474.

A. M. Wodtke, N. Hansen, J. C. Robinson, N. E. Sveum, S. Goncher and D. M. Neumark, "The CI to NCI branching ratio in 248-nm photolysis of chlorine azide," *Chem. Phys. Lett.* 391, 334 (2004).

M. J. Nee, C. Kaposta, A. Osterwalder, C. Cibrian Uhalte, T. Xie, A. Kaledin, S. Carter, J. M. Bowman, D. M. Neumark, and K. R. Asmis, "Experimental and theoretical study of the infrared spectra of BrHI- and BrDI-", *J. Chem Phys.* 121, 7259 (2004).

A. Osterwalder, M. J. Nee, J. Zhou and D. M. Neumark, "High resolution photodetachment spectroscopy of negative ions via slow photoelectron imaging," *J. Chem. Phys.* 121, 6317 (2004).

N. Hansen, A. M. Wodtke, S. J. Goncher, J. C. Robinson, N. E. Sveum, and D. M. Neumark, "Photofragment translation spectroscopy of ClN<sub>3</sub> at 248 nm: Determination of the primary and secondary dissociation pathways" *J. Chem. Phys.* 123, 104305 (2005).

D. M. Neumark, "Probing the transition state with negative ion photodetachment: experiment and theory" *Phys. Chem. Chem. Phys.* 7, 433 (2005).

## 7. Interactions

Gordon Research Conference, Oxford University  
Oxford, London

New Frontiers in Chemical Dynamics and Femtochemistry  
The University of York, Department of Chemistry  
Heslington, York

XIVth Symposium on Atomic, Cluster and Surface Physics  
La Thuile  
Aosta, Italy

227<sup>th</sup> ACS National Meeting  
Anaheim, CA

AFOSR Molecular Dynamics Contractors' Meeting  
New Port, Rhode Island

DICP Symposium on Molecular Dynamics  
Dalian, Liaoning  
P.R. China

AFOSR Contractor's Meeting on Molecular Dynamics/Theoretical Chemistry  
Monterey, CA

Frontiers in Optics  
Laser Science XXI  
Tucson, AZ

Minerva Foundation  
Jerusalem, Israel

40<sup>th</sup> IUPAC Congress  
Beijing, China

230<sup>th</sup> National American Society  
Wanshington, D. C.

**8. New discoveries, invention, or patent disclosures**

(none)

**9. Honors/Awards**

The Optical Society of America, William F. Meggers Award, 2005

Program Chair of Division of Chemical Physics, American Physical Society

Director, Chemical Sciences Division, Lawrence Berkeley National laboratory  
Member of Editorial Advisory Boards:

Journal of Physical Chemistry  
Chemical Physics Letters  
Chemical Physics  
Physical Chemistry Chemical Physics